# Contribution of clinopyroxene EMP and SIMS data to the understanding of magmatic processes: an example from Filicudi

# CONTRIBUTION OF CLINOPYROXENE EMP AND SIMS DATA TO THE UNDERSTANDING OF MAGMATIC PROCESSES: AN EXAMPLE FROM FILICUDI ISLAND (AEOLIAN ARC, SOUTHERN TYRRHENIAN SEA).

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***Abstract*: Clinopyroxenes from basaltic, basaltic andesitic and high-K calc-alkaline andesitic rocks of Filicudi Island (Aeolian Arc, Southern Tyrrhenian Sea) have been investigated by means of Electron Microprobe and Secondary Ion Mass Spectrometry. Texturally these clinopyroxenes can be divided into two groups: 1) euhedral and clear phenocrysts and 2) rounded, dusty or sieved phenocrysts. Both groups span similar compositional range with Wo 34-48, En 38-50 and Fs 4-25. Basalts and basaltic andesites contain clinopyroxene of diopsidic and augitic composition, whereas high-K andesites contain exclusively augite. In terms of major-element concentrations, the phenocrysts exhibit complex variation of Mg, Fe and Ca from core to rim. Clinopyroxene phenocrysts and microphenocrysts display a number of compositional features suggesting disequilibrium with the groundmass. These include: i) Fe/Mg ratios increasing towards the core; ii) wide ranges of some trace elements; and iii) REE contents higher in the core than in the rim. These characteristics suggest a mixing process among magmas of different composition and degree of evolution and support the hypothesis that this process has played an important role during the evolution of Filicudi magmas, as suggested by previously obtained whole rock data.**

Key words: Clinopyroxene, calc-alkaline rocks, Electron Microprobe, Secondary Ion Mass Spectrometry, mixing.

## Introduction

Whole rock chemical data, major and trace element abundances and isotopic ratios, are of primary interest in petrogenetic studies of magmatic rocks. Magmatic minerals are capable of recording details of the history of magma crystallization in their textural and compositional features. Subtle variations in the conditions of crystallization may impose significant compositional variations on crystals (e.g. Pearce and Kolisnik, 1990; Shimizu, 1990). Accordingly, a detailed study of the compositional zonation of minerals may provide information about the change of chemical and physical conditions during crystallization and about evolutionary processes such as magma mixing or crustal contamination. Detailed studies of major and minor element variation in minerals are particularly interesting for island-arc volcanic rocks whose phenocryst abundance is very high.

In this paper, clinopyroxene in calc-alkaline rocks from Filicudi Island in the Aeolian Arc has been investigated by the combined use of conventional petrographic techniques, Electron Microprobe (EMP) and Secondary Ion Mass Spectroscopy (SIMS). The main purpose of this study was to obtain major and trace element abundances in clinopyroxene, to characterize the compositional zoning in this mineral and to discuss the bearing of these data on the processes of the Filicudi magma evolution.

## Geology, Petrography and Petrology

Filicudi Island is located on the western side of the Aeolian Archipelago (Fig. 1), a magmatic arc built up on a 18 km. thick continental crust (Morelli et al., 1975). Detailed geological and petrological studies of Filicudi volcanoes have been recently made by Santo (1990), Francalanci & Santo (1993) and Manetti et al. (1995). A brief summary of the existing data is presented here below.

The island is exclusively made up of volcanic products that were erupted from several centres (Fig.1). Geochronological data (Santo et al., 1995) and field observations indicate that the island was built up through four major phases of volcanic activity during which calc-alkaline lava flows and pyroclastics of basaltic, basaltic-andesitic to high-K andesitic composition were emplaced. The construction of the emergent part of the island began in the present north-eastern sector more than 1 Ma ago. The age of 1.02 Ma (whole rocks 40Ar/39Ar dating; Santo et al., 1995) measured on the

Zucco Grande (Fig. 1) andesitic-basaltic lava flow represents the oldest age found in the Filicudi Island and over the entire Aeolian Island Arc.

In the present work, rock samples from two eruptive centres, Fossa Felci and Fili di Sciacca, were studied. The schematic stratigraphy of these centres and the sampling points are reported in Fig. 2. A brief description of the stratigraphic sequences is as follows (see Manetti et al., 1995 for details).

**Fossa Felci - Volcanic products of this centre span three major eruptive stages starting from 0.39 to 0.04 Ma ago (Santo et al., 1995). During the first period basaltic products were emplaced.** The second stage was characterized by the emission of basaltic, basaltic andesitic and high-K andesitic lavas and pyroclastites. Several dikes with basaltic to basaltic andesitic composition intruded the entire sequence. The emplacement of the andesitic lavas of the Montagnola dome concluded this phase. The third volcanic stage produced pyroclastic deposits rich in clinopyroxene crystals, which extend over the entire island. There is an overall increase in silica with time through the volcanic succession, even though several reversals to more basic compositions (e.g. Fil 82; Fil 85) occur during the second stage.

Fili di Sciacca - This centre was active for a short time during the third major episode of Filicudi volcanic activity. 40Ar/39Ar age obtained from this centre gave a value of 0.19 Ma (Santo et al., 1995). The first volcanic products of this centre represent the most basic volcanics of Filicudi (SiO

Filicudi volcanics display overall similar petrographic and geochemical features. All lava flows have holocrystalline or hypocrystalline textures and a high phenocryst content ranging from 30 to 50% of the total rock volume. Basalts contain plagioclase (plg), clinopyroxene (cpx), and olivine (ol) with rare opaque minerals; basaltic andesites display features similar to those of basalts but with a lower content of olivine which occurs as resorbed microphenocrysts. Small amounts of orthopyroxene (opx) microphenocrysts are also present in basalts and basaltic andesites. High-K andesites show plg as the dominant mineral phase and smaller amounts of cpx and opx. Brown hornblende and biotite occur in the most evolved rocks. Fe-Ti oxide abundance increases passing from basalts and basaltic andesites to high-k andesites. Apatite is present as an accessory mineral and is included in plagioclase and

pyroxene. Generally, the groundmasses consist of the same phases as the phenocrysts. Plagioclase is by far the most abundant mineral. It generally consists of euhedral to subhedral and variously twinned phenocrysts and microphenocrysts, often containing glass or groundmass inclusions. Clinopyroxene occurs as euhedral to subhedral crystals in basalts and as subhedral and anhedral crystals in the more evolved rocks. Phenocrysts show twinning and various inclusions of glass, olivine and oxides. Orthopyroxene, present as euhedral microphenocrysts or phenocrysts, shows a reaction rim to clinopyroxene in some samples. Olivine is generally subhedral and corroded and sometimes exhibits an iddingsitic rim or is mantled by augite in basalts and by opx in basaltic andesites. Hornblende generally shows an opacitic rim. Biotite is often completely transformed into opaque minerals. Finally, Fe-Ti oxides are represented by titanomagmetite and rare ilmenite.

Petrological, geochemical and Sr and Nd isotope compositions suggest fractional crystallization as the main process responsible for the evolution of Filicudi magmas. In fact, least squares mass balance calculations (Stormer & Nicholls, 1978), involving the mineral phases occurring in the Filicudi rocks, successfully reproduce the major element trends (Santo, 1990; Francalanci & Santo, 1993). Nevertheless, several problems arise with trace elements in the modelling, which often does not fit simple fractionation processes. In addition, other geochemical parameters, such as the small but significant variations of Sr and Nd isotope ratios and the relationships between incompatible element abundances and ratios and radiogenic isotope ratios, are also inconsistent with a simple fractionation origin and suggest more complex processes for the evolution of the Filicudi magmas.

## Samples and Analytical Techniques

A total of 17 samples covering the entire compositional range of Filicudi products, from basalts to basaltic andesites up to high-K andesites, was selected for the present study. The sampling points and the composition of the samples studied are reported in the schematic stratigraphic sequences of Fig. 2, in Fig. 3 and in Table 1.

Major element compositions of clinopyroxene were determined by a JEOL JXA-8600 electron microprobe operating at 15 kV and 10 nA and equipped with a Series II Tracor Northern system. Corrections for matrix effects were done according to the method of Bence and Albee (1968). Trace element analyses of selected clinopyroxenes were carried out with a Cameca IMS 4f ion-microprobe at Centro Studio per la Cristallochimica e Cristallografia, University of Pavia (Analysts: Luisa Ottolini and Piero Bottazzi). The techniques used are reported in Shimizu and Hart (1982), Shimizu and Richardson (1987), Bottazzi et al. (1990). Analytical uncertainties are <10% for REE and <5% for the other elements.

Tables 2 and 3 report representative major and trace element analyses of clinopyroxenes.

## Results

Comparison of clinopyroxene analyses of Fili di Sciacca and Fossa Felci rocks reveals no significant difference between them. Consequently, their salient features will be described together.

Cpx phenocrysts are present in all rocks and their modal amount varies between 15% in the basalts and 2% in the evolved rocks. Phenocrysts are generally 1-2 mm in size. Megacrysts of 3-3.5 mm are common in basaltic samples and in a few basaltic andesitic rocks. On the basis of their textures, phenocrysts can be divided into two types: 1) euhedral and clear phenocrysts and 2) rounded, dusty and frittered phenocrysts.

Phenocryst, microphenocryst and groundmass cpxs are commonly Ca-rich and their core compositions lie in the range Wo 38-48, En 38-49, Fs 5-20. Phenocrysts and microphenocrysts in basalts and basaltic andesites have augitic or diopsidic composition (Fig. 4). These two clinopyroxenes sometimes occur together within a single sample or a single crystal. High-K andesites contain more uniform clinopyroxene displaying exclusively augitic composition. The only exception is represented by some phenocrysts found in an andesitic pyroclastic flow (VF4 formation in Fig. 2) emitted during the last eruptive phase of Fossa Felci. In spite of its highly evolved composition, this deposit contains diopsidic clinopyroxene (Fig. 4) displaying high Mg value (80-92; Tab. 2). Therefore, a xenocrystic origin for these phenocrysts can be assumed. In all the sample studied, augite is the only clinopyroxene

in the groundmass. No systematic relation exists between textures and chemical composition of cpx, even if type-1 phenocrysts predominantly display normal zoning and less evolved composition with respect to phenocrysts of type-2.

Major elements - Cpx phenocrysts and microphenocrysts in the Filicudi rocks occur both as zoned and homogeneous crystals. Cpxs of basalts and basaltic andesites show gradual, abrupt or oscillatory zonings. The range of compositional variation in each crystal is generally within 12 mol.% Fs. The most evolved rocks generally contain homogeneous cpx phenocrysts and microphenocrysts. A detailed observation of major-element variations shows: i) crystals displaying a decrease in Ca and Mg and an increase in Fe from core to rim; ii) phenocrysts with rims richer in Mg and Fe than their cores; iii) crystals with Ca and Mg increasing towards the rim and Fe decreasing or nearly constant; and iv) crystals with Mg increasing towards the outer rim while Fe and Ca are constant. Some zoning profiles along representative crystals are reported in Fig. 5. In addition, some examples of core to rim variation in terms of Wo, En and Fs components are shown in Fig. 6.

Fig.7 shows variations of Mg-number (Mg#) for phenocrysts, microphenocrysts and groundmass clinopyroxene in various rock types. Fig. 8 displays the variation of Mg# for specific representative samples. These figures show that phenocryst cores from basalts and basaltic andesites have a wide and similar range of Mg-number (67-90; e.g. Fil 7, Fil 85). Moreover, cores of phenocrysts and microphenocrysts in basalts display a similar range of Mg-number (e.g. Str 199, Fil 76); Mg# of microphenocryst cores in high-K andesites is higher than in the cores of coexisting phenocrysts (e.g Str 171); and, finally, groundmass cpxs show less evolved composition than the microphenocryst rims (e.g. Fil 11, Str 171).

From these Mg# variations two groups of cpx can be distinguished. The first group displays normally zoned crystals, and the second group contains clinopyroxene crystals with more complex characteristics, clearly indicating disequilibrium with the host magma. Similar indications are also given by the features illustrated in Figs. 5 and 6.

Trace elements - Ranges of trace element contents in clinopyroxenes and host whole rocks are reported in Table 4. Cpxs display a wider variability of incompatible trace elements than the corresponding

rocks (Tab. 4 or Figs. 9 and 11). For instance, Zr shows a variation by a factor of 12 in clinopyroxene while whole rocks display a variation by a factor of 3. In addition, a large range of concentrations is also present in a single sample, such as Ti in Fil 11 cpx (970-3000 ppm) or Sr in Fil 86 cpx (45-91 ppm). On the contrary, compatible trace elements like Sc and Cr, show a more restricted range of variation in clinopyroxene than in the corresponding whole rocks. In Fig. 9 a strong scattering of trace element data or a lack of any correlation between major and trace elements are also evident. Instead a good positive correlation exists between compatible (e.g. Sc) and incompatible elements (Fig. 10).

Trace element SIMS data confirm the contemporaneous occurrence of unzoned and variously zoned crystals in the same rock sample. In fact, normally and reversely zoned crystals occur together in rocks such as Fil 11, Fil 7, Str 199. For instance, microphenocrysts display in some cases (e.g. Fil 11) high abundance of Cr while the content of this element is below detection in the coexisting phenocrysts. The occurrence of reversely zoned phenocrysts or microphenocrysts (Fil 10; Fil 85), unzoned (Fil 14) and normally zoned (Str 199) cpx is also evident from Fig. 11, where representative cpx crystals are plotted together with the corresponding whole rocks.

REE patterns of selected cpx phenocrysts and microphenocrysts are reported in Fig. 12. The patterns are those typically found in clinopyroxene and are characterized by increasing abundance of LREE from La to Sm and decreasing or almost flat pattern of HREE; negative Eu anomalies are present in many samples. Several observations can be made, among which: i) some phenocrysts and microphenocrysts have higher REE content in the core than in the rim (e.g. Fil 7, Str 199); ii) some microphenocrysts display lower REE abundance in respect to the associated phenocrysts (e.g Fil 11; Fil 85); iii) Eu anomalies are generally less strong in the microphenocryst rims and in the cpx from the most evolved rocks; and iv) REE zoning is more pronounced in microphenocrysts than in phenocrysts (Fil 85).

## Discussion

The presence in the basalts and basaltic andesites of diopside and augite occurring together in the same sample or within single crystals is an important characteristic of the Filicudi rocks. This feature has

often been observed in calc-alkaline rocks and has been interpreted as evidence for variations in water pressure (e.g. Aurisicchio et al., 1988) or refilling phenomena (Clocchiatti, 1981).

Crystal chemistry studies carried out on the Filicudi cpxs by Malgarotto et al. (1993) have shown that these are characterized by variable polyhedral volumes. This has been interpreted as evidence for polibaric crystallization. Therefore, the contemporaneous presence of diopside and augite with these characteristics in the same rock sample could suggest nucleation at different depth or variable water pressure for the Filicudi crystals.

Some characteristics of the clinopyroxene under study can be explained by considering the hypothesis of magma mixing, occurring in a magma chamber, between residing and newly injected mafic liquids. This process causes a temperature increase of temperature in the magmatic chamber and can induce partial melting of the pre-existing augitic pyroxene and the crystallization of a new diopsidic phase, thus explaining the rounded and reversely zoned crystals as well as the REE variations. Indeed, the higher REE abundance observed in phenocrysts than in microphenocrysts or in the core with respect to the rim (Fig.12) could be also imputed to a separation of a considerable amount of a REE-rich accessory phase such as apatite producing a REE depletion in the melt. However, in the present case, petrographic data indicate that apatite crystallization did not play an important role. Furthermore, change of temperature in the magmatic chamber due to the arrival of a new hotter magma could induce variations in the liquid structure thus modifying partition coefficients and determining the range of incompatible trace element concentration in the cpx to become wider than that found in the liquids. With regard to compatible trace elements, their smaller variability can presumably be imputed to a different or minor effect of temperature on their partition coefficients as suggested by the positive correlation of Fig. 10. However, the variability of the partition coefficient of trace elements with a different degree of compatibility, as a function of T, is not sufficiently known. Alternatively, one can envisage, following Shimizu & Le Roex (1986), that a broad spectrum of melt compositions, not entirely sampled as lavas, occurred in the magma chamber. Evidence in favour of this hypothesis could be the scattering of data observed in the major vs. trace element diagrams (Fig.9).

The contemporaneous presence of crystals displaying and lacking negative Eu anomaly has been imputed to the lack of communication between augite and plagioclase phenocrysts or to the low quantity of plg, not sufficient to produce a negative Eu anomaly (Shimizu & Le Roex, 1986). If this second hypothesis applies to the Filicudi rocks, then the high Eu content could represent additional evidence that some Filicudi clinopyroxenes crystallized under high $P_{H2O}$ conditions, which reducing the plagioclase nucleation, drive the residual liquids to an Al2O3 rich composition (Gust & Perfit, 1986). Moreover, the high Al2O3 and Sr content measured in the groundmasses of some Filicudi basic rocks (Santo et al., 1991, Francalanci & Santo, 1993) also suggests fractionation under high P or high PH2O .

As previously described, Wo, En and Fs contents display complex compositional variations. An increase of Ca content in the latest stage of the cpx growth is not consistent with an equilibrium crystallization (Shimizu & Le Roex, 1986), but if a mixing process is invoked, a new liquid rich in Ca is necessary. In the same way, a rimward increase of En also implies the existence of a liquid richer in Mg than the pre-existing one. In addition, the Mg value distribution of phenocrysts cores, microphenocrysts, and groundmass clinopyroxenes (Figs. 7-8) seems to suggest crystallization of phenocryst cores in distinct magmas having a different evolution degree and possibly several episodes of mixing with nucleation of microphenocrysts and groundmass crystals in the mixed magma. With regard to trace elements, if their wide range of values results from the mixing of several magmas of different composition, taking into account the relationships existing between Sc, Cr and incompatible elements, one would invoke the addition of new liquids whose compatible and incompatible trace element abundances vary sympathetically. Accordingly, it appears unlikely that a simple mixing process alone could be responsible for the major and trace element zoning in clinopyroxene.

The chemical variations observed in the clinopyroxene under investigation seem to point to an important role played by mixing processes during the evolution of these magmas. Additional evidence in favour of this process can be represented by the occurrence of plg of bimodal composition and reversely zoned, of Fo-rich olivine, and An-rich plagioclase which are in disequilibrium with the host glass. The coexistence in some basaltic rocks of olivine and orthopyroxene also points to the same

conclusion. Interestingly, rock samples that record a reversal to a more basic composition along the stratigraphic succession (Fig. 2) are those showing disequilibrium evidence. However, some of these characteristics are also present, though in a minor amount, in other rocks (e.g. Fil 82).

Current interest in the physical characteristics of magma chambers has led to the development of models that assume the existence of magmas with a large spectrum of compositions in a single reservoir and which are available for mixing (Grove et al, 1982). In the case under study, it seems reasonable to assume a model in which the arrival of hot primitive magma in a shallow magmatic chamber causes a temperature increase and therefore a consequent variation in partition coefficients. Consequently, data from Filicudi cpx can be interpreted in terms of mixing between evolved magmas and basic melts of variable composition and containing crystals previously formed at higher pressure or different $P_{H2O}$. According to this model, clinopyroxenes from VF4 formation (Fig. 2) can represent less evolved cpx compositions. Silica variations observed in Fig. 2 thus seem to suggest a cyclic process of arrival of new batches of mafic magma which mix with the evolving magma already present in the magmatic chamber. Thereafter, these processes may be less active with consequent formation of more evolved magmas. In conclusion, magma mixing appears to have occurred at various stages of the evolution of the Filicudi volcanoes. This hybridism is the most plausible model for the interpretation of the mineral chemistry data of Filicudi. This model does not exclude the possibility that some geochemical variations also reflect source characteristics and that other processes could have played a role in the evolution of the Filicudi magmas. In particular, the range of $^{87}Sr/^{86}Sr$ values showing poor correlation with other geochemical parameters (Santo, 1990; Francalanci & Santo, 1993) could suggest a variable addition of crustal components. Finally, evidence coming from the present study calls also for the existence in the Filicudi magma chamber of liquids not sampled as lavas and possibly not directly linked by fractional crystallization to the analysed magmas.

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